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Variation with Temperature of the Recombination of Oxygen Atoms on a Platinum Surface

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THE development of vehicles capable of flight at high Mach speeds and at extreme altitudes has restimulated interest in the "catalytic efficiency" of metals for recombination of atomic species of hydrogen, oxygen, and nitrogen. Most of the work to date has been of an exploratory nature, comparing the relative efficiencies of the different metals.

It is also of paramount importance to know whether the "catalytic efficiency," or more properly, the recombination coefficient γ varies with the temperature of the surface. It is usually tacitly assumed that γ is independent of temperature.[1,2] There is experimental support for this in the case of H atoms: Tollefson and LeRoy[3] have shown that γ for H atoms on Pt is constant between 125 and 450°C; more recently, Fox, Smith, and Smith[4] obtained a similar result for H atoms on Pt and W between 150 and 800°C, though they found a poisoning effect below 150°C.

We have had experience with platinum devices in O atoms and have observed quite a marked change in γ with variation of the temperature of the platinum. The results were obtained with small resistance thermometers similar to some described previously.[5] With these devices, one can measure the joule heating *Wo* developed by the atom recombination occurring on the platinum. *Wo* is directly proportional to the γ of the surface for a given atom concentration. Hence any change in γ with temperature can be detected by measuring *Wo* as the temperature of the wire is altered by electrical heating.

Our measurements indicate that there is a high- and a low-temperature region in which γ is constant, though different, separated by an unstable region. Some of our measurements in the high-temperature region were reported previously[5] and illustrate the consistency of *Wo* in this region. This region extends from 750°C upward. The lower region extends from about 500 down to 150°C. This region is characterized by sluggish behavior, dependence on past history, and poor reproducibility. The experimental values for *Wo* are scattered around a value 0.4 of that for the upper region which indicates that γ is roughly 0.4 of the γ for the upper region. The region between 500 and 750°C is an unstable region. If the platinum reaches a temperature of 500°C, it continues to increase in temperature more and more rapidly until it suddenly lights up well above 750°C. If the temperature is lowered below 750°C, the platinum decreases in temperature until it finally reaches some equilibrium value below 500°C. These results were independent of whether the oxygen was wet or dry.

The results are best explained by assuming that the higher value of γ is characteristic of a Pt surface and that the lower value is characteristic of an oxide surface. The evidence for this is indirect but convincing:

1. As evidence that a platinum surface is not covered with oxide at high temperature, we have shown that a platinum resistance thermometer heated at temperatures above 900°C in a stream of oxygen (pressure of 0.5 mm) remains clean and bright indefinitely while a visible oxide deposit accumulates on the wall of the enclosing tube.[5] Also, we have shown that the rate of oxidation in normal oxygen is directly proportional to the pressure of oxygen.[6] In addition, the literature[7] indicates that the dissociation temperature of both oxides of platinum, $PtO_{(s)}$ and $PtO_{2(s)}$, is 750°C. Under a pressure of 0.5 mm of oxygen, dissociation would be expected to occur at a much lower temperature. We have shown recently from the electron diffraction pattern that the oxide deposit, upon heating to 450°C in a high vacuum, dissociates leaving a residue of metallic platinum.

2. We have demonstrated previously[5] that platinum is oxidized more readily in "activated oxygen" than in normal oxygen, and that the enhanced oxidation occurs with little or no activation energy.[6] Consequently, it appears plausible that even for platinum, a very thin oxide layer can be formed on the metal at a fairly rapid

rate (in an hour or less) at even moderate temperatures (150–500°C) in "activated oxygen."

3. As evidence that O atoms recombine on the oxide, we have observed that the oxide deposits that are formed by the O atoms are sensibly heated by the atoms indicating a fairly high γ. Also, we have shown that the oxide deposit causes a gradual decrease in the number of O atoms indicated by a platinum device even though the output of the discharge tube is constant.[5]

It is uncertain whether the low temperature region is characteristic of a PtO_2 or a PtO surface. It is fairly certain that PtO_2 is formed in normal oxygen.[6] We have some evidence that PtO is formed in "activated oxygen."[8] Also, we find that heating and cooling a platinum device in normal oxygen gives a surface that is very sluggish and unresponsive. However, heating and cooling in the presence of O atoms results in a responsive, active surface. This could be explained by assuming that the active surface characteristic of the low temperature region is a PtO surface and that PtO_2 acts as a poison for this.

Regardless of this, the important point is to emphasize the variability of the surface with temperature. If a Pt surface can oxidize in "activated oxygen," it seems reasonable to assume that other metals would be readily covered with a thin film of oxide. Grey and Darby[9] have found evidence for this with several metals, and Greaves and Linnett[10] explain their results on this assumption. As oxides are often subject to variable valences, phase changes, dissociation, volatilization, etc., upon heating, it would seem reasonable to predict that the recombination coefficient for O atoms on most metals would in general not be constant but would be temperature dependent.

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